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(21) International Application Number: PCT/GB82/00118 (22) International Filing Date: 21 April 1982 (21.04.82) (31) Priority Application Numbers: 258,733 8203701 (32) Priority Dates: 29 April 1981 (29.04.81) 9 February 1982 (09.02.82) (33) Priority Countries: US GB (60) Parent Application of Grant (63) Related by Continuation US 258,733 (CIP) Filed on 29 April 1981 (29.04.81) (71) Applicant (for all designated States except US): DAVY McKEE (LONDON) LIMITED [GB/GB]; 250 Eus- ton Road, London NW1 2PG (GB).	(72) Inventors; and (75) Inventors/Applicants (for US only): BRADLEY, Mi- chael, William [GB/GB]; 52 Trefoil Wood, Marton, Middlesbrough, Cleveland (GB). HARRIS, Norman [GB/GB]; 22 Grantham Road, Norton, Cleveland (GB). TURNER, Keith [GB/GB]; 12 The Avenue, Fairfield, Stockton-on-Tees, Cleveland (GB). (74) Agent: EYLES, Christopher, Thomas; Batchellor, Kirk & Eyles, 2, Pear Tree Court, Farringdon Road, Lon- don EC1R ODS (GB). (81) Designated States: AT, AU, BR, DE, DK, FI, GB, JP, KP, NL, NO, SE, US. Published <i>With international search report.</i>	
(54) Title: PROCESS FOR HYDROGENOLYSIS OF CARBOXYLIC ACID ESTERS (57) Abstract A process for effecting hydrogenolysis of a carboxylic acid ester comprising contacting a vaporous mixture contain- ing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm ² absolute (about 9.8 kPa) up to about 100 kg/cm ² absolute (9813 kPa).		

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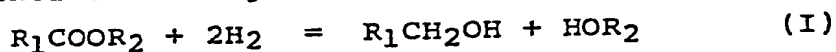
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PROCESS FOR HYDROGENOLYSIS OF CARBOXYLIC ACID ESTERS

This invention relates to the hydrogenolysis of carboxylic acid esters.

Hydrogenolysis of carboxylic acid esters has been described on numerous occasions in the literature. Typically in such a reaction the -CO-O- linkage of the ester group is cleaved so that the acid moiety of the ester group is reduced to an alcohol whilst the alcohol moiety is released as free alcohol according to the following equation:



where R_1 and R_2 are each alkyl radicals, for example. According to page 129 et seq of the book "Catalytic Hydrogenation in Organic Synthesis" by M. Freifelden, published by John Wiley and Sons Inc (1978), the catalyst of choice for this reaction is said to be barium promoted copper chromite. Typical reaction conditions include use of temperatures in the region of 250°C and pressures in the range of 225-250 atmospheres (about 22.81 MPa to about 25.35 MPa). Although a good yield of alcohol is often obtained using this technique for hydrogenolysis of an ester, the temperature necessary for conversion of the ester to alcohol is also conducive to side reactions. For example, the resulting alcohol may undergo further hydrogenolysis to hydrocarbon or may react with starting material to produce a higher molecular weight ester that is more difficult to hydrogenolyse.

Besides these side reactions copper chromite catalysts have other disadvantages for commercial scale operation. In particular, the use of copper chromite catalysts is environmentally hazardous and necessitates the adoption of special and costly handling techniques on account of the toxicity of chromium. Moreover it is difficult to produce successive batches of copper chromite with reproducible catalyst activity.

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United States Patent Specification No. 2079414 describes a process for catalytic hydrogenation of esters using catalysts such as fused copper oxide, either wholly or partially reduced, which may be promoted with oxide promoters such as manganese oxide, zinc oxide, magnesium oxide or chromium oxide. Particularly recommended catalysts are those comprising copper oxide promoted by chromium oxide, e.g. copper chromite. According to page 3, right-hand column line 57 et seq.: "In operating in the vapour phase it is preferred to use temperatures within the range of 300°C to 400°C". It is also stated that: "The best conversions to alcohols are obtained at the highest pressures obtainable in the available equipment and at the lowest temperatures consistent with obtaining a practical rate of reaction" (page 4, right hand column, line 2 et seq.). The Examples describe batch reactions and in all cases the pressure is 2500 psia or higher (17250 kPa or higher), whilst in all cases the temperature is 250°C or higher; in most cases it exceeds 300°C. A limitation to the process is that methyl esters cannot be used because methanol, which would be a hydrogenation product from a methyl ester, is subject to gaseous decomposition (see page 5, right hand column, line 58 et seq.). Similar considerations would appear to prevent the application of the process to esters of formic acid since the formic acid moiety would also be likely to yield methanol.

Further teaching of the use of chromites as catalysts for hydrogenation of esters will be found in United States Patent Specification No. 2109844.

Example 4 of United States Patent Specification No. 3197418 discloses the preparation of a copper-zinc catalyst which can be used in the liquid phase hydrogenation of oils and fats at pressures in excess of 120 kg/cm² (11776 kPa) and at a temperature of 320°C.

United States Patent Specification No. 2241417 teaches the production of higher aliphatic alcohols by liquid

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phase hydrogenation of glycerides in the presence of copper-containing catalysts at temperature of 200°C to 400°C and at pressures of 60 to 500 atmospheres (5884 to 49033 kPa).

Hydrogenolysis of esters to saturated hydrocarbons using catalysts having as essential ingredients an indium or rhodium component and a halogen component is described in United States Patent Specification No. 4067900.

Catalytic hydrogenolysis of formate esters present in oxo reaction products using Ni catalysts is described in East German Patent Specification No. 92440 (see Chem. Abs., 124069j, Vol 78 (1973), page 439). Other references to hydrogenation of formates include a paper by E. Lederle, Anales Real Soc. Espan. Fis. y Quim. (Madrid) 57B, pages 473-5 (1961). Also West German Patent Specification No. 902375 describes the production of methanol by hydrogenation of alkyl formates at pressures of 20 to 50 atmospheres (1961 to 4903 kPa) using copper chromite catalysts; there is a passing suggestion to incorporate zinc oxide in the catalyst.

Catalytic cleavage of formic acid esters is described in British Patent Specification No. 1277077. According to this proposal a hydrogenation catalyst containing copper and nickel is used but the formyl radical is reported to be dehydrogenated in the course of the reaction and appears as carbon monoxide.

Production of ethylene glycol by hydrogenolysis is suggested by some references including United States Patent Specification No. 4113662 which teaches hydrogenation of esters to alcohols at temperatures of 150°C to 450°C and pressures of 500-10,000 psig (3450-69000 kPa) using catalysts comprising cobalt, zinc and copper. Examples IV, V and VIII describe comparative experiments using polyglycolide and methyl glycolate with Cu-Zn oxides as catalyst at 250°C and at pressures of at least 2800 psig (19421 kPa), i.e. conditions under which the ester (polyglycolide or methyl

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glycolate) is in the liquid phase. United States Patent Specification No. 2305104 describes hydrogenation of alkyl glycolates using catalysts containing Zn, Cr, and Cu to produce ethylene glycol. Vapour phase hydrogenation of oxalate esters at temperatures of 150°C to 300°C for the production of ethylene glycol has been described in United States Patent Specification No. 4112145; this process uses a copper chromite or copper zinc chromite catalyst and requires that the oxalate ester has a sulphur content of less than 0.4 ppm.

It would be desirable to provide a process for effecting hydrogenolysis of esters with negligible formation of by-products or of "heavies" which can be effected under mild conditions.

It would further be desirable to provide a process for effecting hydrogenolysis of formate esters and of methyl esters without significant decomposition of product methanol in the course of the reaction.

It would also be desirable to provide a hydrogenolysis process which utilises a simple catalyst that can be prepared with reproducible catalyst activity.

The present invention accordingly seeks to provide an improved process for effecting hydrogenolysis of esters which can be effected under mild conditions.

The invention further seeks to provide a process for effecting hydrogenolysis of formate esters to give high yields of methanol at high conversions.

It also seeks to provide a process for the production of ethanol by effecting hydrogenolysis of acetate esters in high yield and at high conversions under mild conditions.

Yet again the invention seeks to provide improved processes for the production of ethylene glycol starting from oxalic acid esters or from glycolic acid esters utilising catalytic hydrogenolysis under mild conditions.

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The invention additionally seeks to provide novel hydrogenolysis routes to diols, such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, and 1,6-hexanediol, starting from diesters of dicarboxylic acids or monoesters of hydroxycarboxylic acids.

In addition the invention seeks to provide a process for effecting hydrogenolysis of methyl esters and of formate esters under mild conditions such that decomposition of significant amounts of product methanol under the reaction conditions employed is substantially avoided.

It is also an aim of the invention to provide an improved method of producing 1,4-butanediol by hydrogenolysis of butyrolactone.

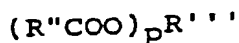
According to the present invention there is provided a process for effecting hydrogenolysis of a carboxylic acid ester which comprises contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa).

The ester may be essentially any vaporisable ester. Amongst esters that may be mentioned are the esters of mono-, di- and polycarboxylic acids which may be derived from mono-, di- or poly-ols.

As examples of suitable esters there may be mentioned those of the general formula:



as well as those of the general formula:



In the above general formulae n and p each represent an integer, preferably an integer of from 1 to about 5, e.g. 1, 2 or 3, and R , R' , R'' and R''' each represent an optionally substituted saturated or unsaturated cyclic or acyclic

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hydrocarbon radical, one or more carbon atoms of which may be replaced by hetero atoms, such as nitrogen, oxygen, or phosphorus. Examples of possible substituents on the radicals R, R', R'' and R''' include oxygen atoms as well as hydroxy and alkoxy groups. Preferably R, R', R'' and R''' each contain from 1 to about 12 carbon atoms. Typically R, R', R'' and R''' are selected from alkyl, alkenyl, alkoxyalkyl, hydroxyalkyl, aryl, aralkyl, alkylaryl, alkoxyaryl, hydroxyaryl, cycloalkyl, alkylcycloalkyl, alkoxyalkyl, hydroxycycloalkyl and cycloalkyl radicals

Such esters may be derived from the following acids:

- formic acid;
- acetic acid;
- propionic acid;
- n- and iso-butyric acids;
- n- and iso-valeric acids;
- caproic acid;
- caprylic acid;
- capric acid;
- 2-ethylhexanoic acid;
- glycolic acid;
- pyruvic acid;
- cyclohexane carboxylic acid;
- benzoic acid;
- o-, m- and p- toluic acids;
- o-, m- and p-methoxybenzoic acids;
- naphth-2-oic acid;
- cinnamic acid;
- oxalic acid;
- malonic acid;
- succinic acid;
- glutaric acid;
- adipic acid;
- maleic acid;

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fumaric acid;
acrylic acid;
methacrylic acid;
alpha- or beta-crotonic acid;
acetylene-dicarboxylic acid;
methoxyacetic acid;
phenylacetic acid;
vanillic acid;
terephthalic acid;
o-salicylic acid;
lactic acid;
citric acid;
gamma-hydroxybutyric acid;
furoic acid; and the like.

Preferably the acid contains from 1 to about 12 carbon atoms.

Suitable mono-, di- or polyols may be selected from:

methanol;
ethanol;
n- or iso-propanol;
n-, iso-, sec- or t-butanol;
pentan-1- or -2-ol;
2-methyl-butan-2-, -3- or -4- ol;
hexanols;
heptanols;
octanols (e.g. 2-ethyl-hexanol);
cetyl alcohol;
lauryl alcohol;
furfuryl alcohol;
ethylene glycol;
1,2- or 1,3-propylene glycol;
1,4-butanediol;
1,6-hexanediol;
glycerol;

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allyl alcohol;
vinyl alcohol;
phenol;
o-, m- or p- cresol;
benzyl alcohol;
phenylethyl alcohol;
ethylene glycol monomethyl ether;
ethylene glycol monoethyl ether;
cyclohexanol;

mono-, di-, and tri-ethanolamine; and the like.
Preferably the mono, di- or polyol contains not more than about 12 carbon atoms.

As examples of specific esters there may be mentioned:

alkyl formates (e.g. methyl, ethyl, n- and iso-propyl, n-, iso-, sec- and t-butyl formates);
alkyl acetates (e.g. methyl, ethyl, n- and iso-propyl, and n-, iso-, sec- and t-butyl acetates);
cycloalkyl acetates (e.g. cyclohexyl acetate);
alkyl propionates (e.g. n-propyl propionate);
alkyl n-butyrates (e.g. n-butyl n-butyrate);
alkyl iso-butyrates (e.g. iso-butyl iso-butyrate);
alkyl n-valerates (e.g. n-amyl valerate);
alkyl iso-valerates (e.g. methyl iso-valerate);
alkyl caproates (e.g. ethyl caproate);
alkyl caprylates (e.g. methyl caprylate);
alkyl caprates (e.g. ethyl caprate);
alkyl 2-ethylhexanoates (e.g. 2-ethylhexyl 2-ethylhexanoate);
vinyl acetate;
allyl acetate;
alkyl alkoxyacetates (e.g. methyl methoxyacetate);
alkyl glycolates (e.g. methyl and ethyl glycolates);
dialkyl oxalates (e.g. dimethyl, diethyl and

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di-n-butyl oxalates);
dialkyl succinates (e.g. dimethyl and diethyl...
succinates);
dialkyl adipates (e.g. dimethyl and diethyl
adipates);
ethylene glycol mono- and di-carboxylates (e.g.
ethylene glycol diformate, ethylene glycol mono-
and di-acetates, ethylene glycol di-n-butyrate,
ethylene oxalate, ethylene glycol glycolate);
monocarboxylic acid esters of furfuryl alcohol
(e.g. furfuryl acetate);
alkyl esters of aromatic acids (e.g. methyl
benzoate, ethyl benzoate, methyl o-toluate,
methyl naphth-2-oate, methyl phenylacetate,
ethyl phenylacetate);
phenyl esters of monocarboxylic acids (e.g. phenyl
acetate);
benzyl esters of monocarboxylic acids (e.g. benzyl
acetate);
dialkyl maleates (e.g. dimethyl maleate, diethyl
maleate);
dialkyl fumarates (e.g. dimethyl fumarate, diethyl
fumarate);
dialkyl esters of acetylene-dicarboxylic acid (e.g.
dimethyl acetylene-dicarboxylate);
dialkyl malonates (e.g. diethyl malonate);
alkyl glycolates (e.g. methyl glycolate, ethyl
glycolate);
alkyl lactates (e.g. ethyl lactate);
alkyl pyruvates (e.g. ethyl pyruvate);
alkyl cyclohexanecarboxylates (e.g. methyl
cyclohexanecarboxylate);
lactones (e.g. gamma-butyrolactone); and the like.

In the process of the invention the vaporous
mixture to be contacted with the catalyst contains, in

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addition to the ester, hydrogen either alone or in admixture with other gases (desirably gases inert to the ester and the catalyst). The gaseous mixtures containing hydrogen include inert gases such as nitrogen, or carbon monoxide.

The term "hydrogen-containing gas" as used herein includes both substantially pure hydrogen gas as well as gaseous mixtures containing hydrogen.

The hydrogenolysis process of the present invention is conducted at a temperature of between about 75°C and about 300°C; although in many cases the preferred temperature may lie in the range of from about 150°C to about 200°C, e.g. with alkyl formates, in most cases it typically is between about 180°C and about 240°C. In some cases a lower range may be preferred; for example, with t-butyl formate the preferred temperature range is from about 130°C to about 190°C. The total pressure is between about 0.1 kg/cm² absolute (about 9.8 kPa) and about 100 kg/cm² absolute (about 9813 kPa), preferably not more than about 50 kg/cm² absolute (about 4906 kPa), and even more preferably between about 5 kg/cm² absolute (about 491 kPa) and about 25 kg/cm² absolute (about 2453 kPa).

The mixture of CuO and ZnO, before reduction, preferably contains from about 5 to about 95 percent by weight, typically from about 10 to about 70 percent by weight, of CuO and from about 95 to about 5 percent by weight, typically from about 90 to about 30 percent by weight, of ZnO. Hence the mixture may contain, for example, from about 20 to about 40 percent by weight of CuO and from about 60 to about 80 percent by weight of ZnO. A preferred mixture, for example, comprises from about 30 to about 36 percent by weight of CuO and from about 62 to about 68 percent by weight of ZnO. Other particularly preferred mixtures comprise from about 65 to about 85 percent by weight of CuO and from about 35 to about 15 percent by weight of ZnO, for example mixtures comprising from about 68 to about

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75 percent by weight of CuO and from about 32 to about 25 percent by weight of ZnO. The hydrogenolysis catalyst may contain minor amounts of other materials such as carbon, sodium, titanium, zirconium, manganese, silica, diatomaceous earth, kieselguhr, and aluminium oxide. Such other materials do not usually comprise more than about 20 percent by weight calculated (except in the case of carbon) as oxide. In the case of sodium it is best not to exceed about 0.5 percent by weight, calculated as oxide. Hence other preferred catalysts include mixtures comprising from about 40 to about 50 weight percent each of CuO and ZnO and from 0 to about 20 weight percent of alumina. The catalyst is, however, preferably essentially free from other metals, particularly from metals of Group VIII of the Periodic Table, such as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt, as well as from Group VIB metals, such as Cr, Mo, and W, from the metals Tc, Ag, Re, Au and Cd, and also from elements of atomic number 80 and above, e.g. Hg and Pb. By the term "essentially free" we mean that the catalyst contains not more than about 0.1 wt% (i.e. not more than about 1000 ppm), and preferably not more than about 250 ppm, of the element in question. The catalyst may be prepared by any of the methods known in the art of forming a composite of copper oxide and zinc oxide. The catalyst may be prepared by fixing the separate oxides, by coprecipitation of the oxalates, nitrates, carbonates, or acetates, followed by calcination. The coprecipitation method is preferred. Generally, the mixture of CuO and ZnO is reduced by hydrogen or carbon monoxide at a temperature in the range of between about 160° and about 250°C for several hours, preferably for 8 to 24 hours, prior to contact with the vaporous mixture containing ester and hydrogen. If the catalyst is charged in a pre-reduced form the period required for reduction can be reduced accordingly.

The mixture of CuO and ZnO is reduced prior to its

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use as catalyst in the hydrogenolysis step. Hydrogen or CO, or mixtures thereof, are generally mixed with a diluent gas such as steam, nitrogen, or combustion gas, to maintain the catalyst bed temperature and to carry away the heat of reduction.

Reduction of the mixture of CuO and ZnO is complete when no more hydrogen or carbon monoxide is being reacted as shown by analysis of the inlet and outlet gas. When using hydrogen complete reduction of the mixture occurs when the total amount of water produced in the reduction is equal to the stoichiometric value of water which should be produced when a given amount of copper oxide is reduced to copper. This value is about 0.079 kg of water per kg of catalyst for a mixture containing 35 weight percent of CuO.

An inert carrier material may be included in the hydrogenolysis catalyst composition. The catalyst is generally formed into pellets, tablets, or any other suitable shape prior to use, by conventional techniques.

It is advantageous that the mixture of CuO and ZnO have an internal surface area of from about 25 to about 50 sq.m. per gram. The internal surface area may be determined by the well-known BET method.

The process of the present invention is most conveniently carried out in a continuous manner, although semi-continuous or batch operations may also be employed. In the preferred method of continuous operation, an ester, or a mixture of esters, a hydrogen containing gas, and optionally, a carrier gas such as nitrogen, may be brought together and, under the desired pressure contacted in the vaporous state with the catalyst. The reaction zone advantageously is an elongated tubular reactor wherein the catalyst is positioned.

In the hydrogenolysis process of the invention the primary reaction observed with many esters is that of equation (I) above. Hence a monocarboxylic ester in this case yields a mixture of alcohols, one derived from the

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carboxylic acid moiety and one derived from the alcohol moiety. Esters of dicarboxylic acids and those derived from polyols give corresponding di- and polyols. Thus, for example, dialkyl oxalates yield ethylene glycol and the corresponding alkyl alcohol. In some cases, however, the products include hydrocarbons derived either from the carboxylic acid moiety or from the alcohol moiety or both. Presumably the alcohols are first formed but are then rapidly hydrogenated to the corresponding hydrocarbon under the reaction conditions used. Under normal operating conditions alcohols are the major products when alkyl esters of aliphatic acids are employed as feedstock. However, when using esters of aromatic acids, such as benzoic acid, or of aromatic alcohols, such as benzyl alcohol, the major product derived from the aromatic acid moiety, or from the aromatic alcohol moiety, as the case may be, is usually the corresponding hydrocarbon.

In some cases an alcohol produced as primary product may undergo further reaction. For example, hydrogenolysis of diethyl maleate or of diethyl succinate may yield not the 1,4-butanediol perhaps to be expected as primary product but tetrahydrofuran. Moreover in hydrogenolysis of t-butyl acetate the observed products contain not only t-butyl alcohol but also iso-butene, presumably formed by dehydration of t-butanol under the reaction conditions used.

The alcohol and/or hydrocarbon product or products (if liquefiable) from the hydrogenolysis reaction may be separated from the hydrogen by condensation and the excess hydrogen can be compressed and recycled to the reaction zone. The crude alcohol or hydrocarbon product may be used in this form or it can be further purified in a conventional manner such as by fractional distillation. If desired, any unconverted portion of the ester or ester mixture may be separated from the reaction product and recycled to the

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reaction zone and, preferably, admixed with fresh feed gases prior to entering the reaction zone.

In operating the process of the invention the partial pressure of the ester may vary within wide limits, e.g. from about 0.05 kg/cm² (4.9 kPa) or less up to about 10 kg/cm² (981 kPa) or more. Care must however be taken to ensure that at all times the temperature of the vaporous mixture in contact with the catalyst is above the dew point of the ester under the prevailing pressure conditions.

The vaporous mixture preferably contains at least an amount of hydrogen corresponding to the stoichiometric quantity of hydrogen required for hydrogenolysis. Usually an excess of hydrogen over the stoichiometric quantity will be present. In this case the excess hydrogen remaining after product recovery can be recycled to the catalytic reaction zone. As will be apparent from equation (I) above, 2 moles of hydrogen are required for hydrogenolysis of each carboxylic acid ester group present in the ester molecule. If the ester contains non-aromatic unsaturation (i.e. carbon-carbon double or triple bonds) such unsaturated linkages may also undergo hydrogenation under the hydrogenolysis conditions employed. Hence the stoichiometric quantity of hydrogen required for reduction of 1 mole of an unsaturated mono-ester may correspond to 3, 4 or more moles of hydrogen.

Diesters require 4 moles of hydrogen per mole of diester, if saturated, for hydrogenolysis; non-aromatically unsaturated diesters may require 5 or more moles of hydrogen for hydrogenolysis of 1 mole of diester. Triesters and higher polyesters will require 6 or more moles of hydrogen, depending upon the number of ester groups and non-aromatic unsaturated bonds, per mole for hydrogenolysis.

The hydrogen:ester molar ratio within the vaporous mixture may vary within wide limits, e.g. from about 2:1 to about 100:1 or more for a monoester or from about 4:1 to



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about 100:1 or more for a diester. This ratio will depend, at least to some extent, on the volatility of the ester used as well as on the number of ester groups in the ester substrate to be reduced. Typically the hydrogen:ester molar ratio is at least about 25:1.

Although the process of the invention is generally applicable to carboxylic acid esters best results will usually be obtained with esters boiling at temperatures of not more than about 300°C at atmospheric pressure. Whilst it is possible to utilise esters having still higher boiling points, the use of higher boiling point materials limits the partial pressure of the ester that can be used in the vaporous mixture and hence limits the rate of hydrogenolysis. If extremely high boiling esters are used then rates of reaction will be correspondingly reduced.

Certain esters may undergo thermal decomposition at temperatures approaching 300°C and possibly at temperatures below their boiling point at atmospheric pressure. When using such esters the temperature during hydrogenolysis should not be so high that significant thermal decomposition of the ester occurs.

In general it is preferred to use monocarboxylic acid esters, preferably aliphatic monocarboxylic acid esters of aliphatic alcohols, containing from 2 to about 20 carbon atoms, or dicarboxylic acid diesters, preferably aliphatic dicarboxylic acid diesters, containing from 4 to about 16 carbon atoms.

According to a particularly preferred aspect of the invention there is provided a process for the production of ethylene glycol which comprises effecting hydrogenolysis of an oxalic acid ester by contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm²

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absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting ethylene glycol. In the hydrogenolysis of oxalic acid esters the use of temperatures of from about 180°C to about 240°C is preferred; preferred operating pressures range from about 5 kg/cm² absolute (about 491 kPa) up to about 35 kg/cm² absolute (about 3435 kPa).

According to another preferred aspect of the present invention there is provided a process for the production of methanol which comprises effecting hydrogenolysis of a formic acid ester by contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting methanol. In the hydrogenolysis of formic acid esters to produce methanol the temperature preferably ranges from about 130°C to about 220°C, e.g. from about 150°C to about 190°C, and the pressure ranges preferably from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

According to a still further aspect of the present invention there is provided a process for the production of ethanol which comprises effecting hydrogenolysis of an acetic acid ester which comprises contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting ethanol. In the hydrogenolysis of acetic acid esters to produce ethanol the temperature preferably ranges from about 180°C to about 240°C

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and the pressure from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

The invention further provides a process for the production of 1,4-butanediol and/or tetrahydrofuran which comprises effecting hydrogenolysis of an ester of an acid selected from maleic acid, fumaric acid, acetylenedicarboxylic acid, and succinic acid, by contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting 1,4-butanediol and/or tetrahydrofuran. In the production of 1,4-butanediol and/or tetrahydrofuran by such a process it is preferred that the temperature should be between about 180°C and about 240°C whilst the preferred pressure range is from about 5 kg/cm² absolute (about 491 kPa) up to about 35 kg/cm² absolute (about 3435 kPa).

In accordance with the invention there is also provided a process for the production of ethylene glycol which comprises effecting hydrogenolysis of a glycolic acid ester by contacting a vaporous mixture containing the ester and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting ethylene glycol. In the hydrogenolysis of glycolic acid esters to produce ethylene glycol it is preferred to operate at from about 180°C to about 240°C and to use pressures of from about 5 kg/cm² absolute (about 491 kPa) up to about 35 kg/cm² absolute (about 3435 kPa).

There is further provided a process for the production of 1,4-butanediol which comprises effecting



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hydrogenolysis of butyrolactone by contacting a vaporous mixture containing butyrolactone and hydrogen with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and recovering resulting 1,4-butanediol. In the hydrogenolysis of butyrolactone it is preferred to use a temperature in the range of from about 180°C to about 240°C and a pressure in the range of from about 5 kg/cm² absolute (about 491 kPa) up to about 45 kg/cm² absolute (about 4416 kPa). Best yields of 1,4-butanediol are generally achieved towards the higher end of the pressure range, for example, when the pressure is in the range of from about 25 kg/cm² absolute (about 2453 kPa) up to about 45 kg/cm² absolute (about 4416 kPa).

In each case recovery of the hydrogenolysis products can be effected in conventional manner, e.g. by condensation followed, if desired, by fractional distillation under normal, reduced or elevated pressure.

The invention is further illustrated in the following Examples.

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Example 1

n-butyl butyrate was pumped at a rate of 3.8 ml/hr to an electrically heated gas/liquid mixing device to which hydrogen was also supplied at a controlled rate and pressure. The resulting vaporous mixture was passed through a lagged, electrically heated line to a pre-heating coil prior to passage through a tubular reactor packed with 146 ml of a powdered catalyst. Both the tubular reactor and the pre-heating coil were immersed in a molten salt bath which was heated to 174°C. The vaporous mixture exiting the reactor was passed through a water cooled condenser and the resulting condensate was collected in a water-cooled knock out pot. The exit gas pressure was controlled to 10.55 kg/cm² absolute (1035 kPa). The non-condensed gases were then passed through a let-down valve, the gas flow rate being monitored downstream from this valve in a wet gas meter. A gas flow rate of 46.4 litres/hr (measured at atmospheric pressure) was maintained throughout the experiment.

The liquid condensate was analysed by gas chromatography using a 2 metre stainless steel column (6 mm outside diameter) packed with polyethylene glycol (nominal molecular weight 20,000) on Chromosorb PAW, a helium gas flow rate of 30 ml/minute and a flame ionisation detector. The instrument was fitted with a chart recorder having a peak integrator and was calibrated using a mixture of n-butanol and n-butyl butyrate of known composition. The condensate was shown to contain a mixture of 99.62 wt % butanol and 0.28 wt % n-butyl butyrate, corresponding to a 99.7% conversion with essentially 100% selectivity.

The catalyst used in this Example was charged to the reactor as a co-precipitated mixture of CuO and ZnO containing 33⁺³% CuO and 65⁺³% ZnO having a particle size in the range of 1.2 mm to 2.4 mm and an internal surface area of about 45 sq. m. per gram. This was pre-reduced in the reactor using a 5 vol % H₂ in N₂ gas mixture at 200°C for

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17 hours followed by pure hydrogen at 200°C for 8 hours, the gas flow rate in each case being about 20 litres/hr (measured at atmospheric pressure using the wet gas meter) and the gas pressure being 10.55 kg/cm² absolute (1035 kPa). After this pre-reduction stage the catalyst was at all times maintained in a hydrogen-containing atmosphere.

Example 2

The procedure of Example 1 was repeated using ethyl acetate in place of n-butyl butyrate at a feed rate of 7.4 mls/hr and a hydrogen flow rate of 41.9 litres/hr (measured at atmospheric pressure by means of the wet gas meter). In this experiment the salt bath temperature was 185°C and the exit gas pressure was 10.55 kg/cm² absolute (1035 kPa). The liquid condensate was shown to contain a minor amount of ethyl acetate, a major amount of ethanol and a trace of n-butanol. The observed conversion to ethanol was 97.1% and the selectivity to ethanol was about 95%.

Example 3

When the procedure of Example 2 was repeated at a salt bath temperature of 203°C, with a gas flow rate of 160.4 litres/hr and a liquid feed flow rate (of ethyl acetate) of 34.8 ml/hr, both ethyl acetate and ethanol were identified in the liquid condensate but essentially no n-butanol was formed. The conversion of ester was 82.6% and the selectivity to ethanol was approximately 100%.

Example 4

The procedure of Example 1 was followed using iso-propyl formate, which was supplied at a rate of 23.4 ml/hr, and a gas flow rate of 35.1 litres/hr (as measured at atmospheric pressure by the wet gas meter). The salt bath temperature was 185°C and the exit gas pressure was 10.55 kg/cm² absolute (1035 kPa). The liquid condensate was analysed and shown to contain as major components, besides minor trace amounts of acetone and butanol, methanol and iso-propyl alcohol. The conversion of ester starting



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material was essentially 100% and the selectivity to methanol was approximately 99%.

Example 5

The procedure of Example 1 was repeated using methyl acetate in place of n-butyl butyrate at a feed rate of 75 mls/hr and a hydrogen flow rate of 115.2 litres/hr (measured at atmospheric pressure). In this experiment the salt bath temperature was 194°C and the exit gas pressure was 9.49 kg/cm² absolute (935 kPa). The liquid condensate was shown to contain 55.7 wt% methyl acetate, 10.02 wt% ethyl acetate, 15.24 wt% ethanol, and 18.95 wt% methanol. The observed conversion to ethanol was 52.4 mol%.

Example 6

The procedure of Example 5 was repeated at a salt bath temperature of 217°C with an exit gas pressure of 8.86 kg/cm² absolute (868 kPa), with a gas flow rate of 225 litres/hr, and with a liquid feed flow rate (of methyl acetate) of 75 ml/hr. The liquid condensate was shown to contain 19.31 wt% methyl acetate, 11.19 wt% ethyl acetate, 35.64 wt% ethanol, and 31.96 wt% methanol. The observed conversion to ethanol was 72.40 mol%.

Example 7

The procedure of Example 1 was repeated using sec-butyl acetate in place of n-butyl butyrate at a feed rate of 118 mls/hr and a hydrogen flow rate of 143.9 litres/hr (measured at atmospheric pressure). In this experiment the salt bath temperature was 203°C and the exit gas pressure was 10.55 kg/cm² absolute (1035 kPa). The liquid condensate was shown to contain 6.0 wt% ethyl acetate, 20.6 wt% ethanol, 40.1 wt% sec-butyl acetate, and 33.3 wt% sec-butanol. The observed conversion to ethanol was 59.9 mol% and the selectivity to ethanol and sec-butanol was essentially 100%.

Example 8

Di-n-butyl oxalate was pumped at a rate of 15.4 ml/hr to an electrically heated gas/liquid mixing device to



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which hydrogen was also supplied at a controlled rate and pressure via an electrically heated line. The resulting vaporous mixture was passed through a lagged, electrically heated line to a pre-heating coil prior to passage through a tubular stainless steel reactor packed with 15 ml of a crushed catalyst. Both the tubular reactor and the pre-heating coil were immersed in a molten salt bath. The temperature of the salt bath was adjusted until the temperature of the vaporous mixture, as detected by a thermocouple positioned immediately upstream from the catalyst bed, was 240°C. The vaporous mixture exiting the reactor was passed through a water cooled condenser and then through a second refrigerated condenser through which coolant at -15°C was passed. The resulting condensate was collected in a refrigerated knock out pot also kept at -15°C. The exit gas pressure was controlled to 15.5 kg/cm² absolute (1518 kPa). The non-condensed gases were then passed through a let-down valve, the gas flow rate being monitored downstream from this valve in a wet gas meter. A gas flow rate of 156.6 litres/hr (measured at atmospheric pressure) was maintained throughout the experiment. The liquid space velocity of the di-n-butyl oxalate was 1.03 hr⁻¹.

The liquid condensate was analysed by gas chromatography using a 2 metre stainless steel column (6mm outside diameter) packed with polyethylene glycol (nominal molecular weight 20,000) on Chromosorb PAW, a helium gas flow rate of 30 ml/minute and a thermal conductivity detector. The instrument was fitted with a chart recorder having a peak integrator and was calibrated using a mixture of ethanol, n-butanol, ethyl glycolate, n-butyl glycolate, ethylene glycol and di-n-butyl oxalate of known composition. The condensate was shown to contain a mixture of 0.60 wt% ethanol, 31.37 wt% n-butanol, 0.1 wt% ethyl glycolate, 0.7 wt% n-butyl glycolate, 15.88 wt% ethylene glycol, and 70.15 wt% n-butyl oxalate, corresponding to a 27.5% conversion with

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93.0% selectivity to ethylene glycol.

The catalyst used in this Example was charged to the reactor as a co-precipitated mixture of CuO and ZnO containing $33 \pm 3\%$ CuO and $65 \pm 3\%$ ZnO having a particle size in the range of 1.2 mm to 2.4 mm and an internal surface area of about 45 sq.m. per gram. This was pre-reduced in the reactor using a 5 vol % H₂ in N₂ gas mixture at 200°C for 16 hours followed by pure hydrogen at 200°C for 16 hours, the gas flow rate in each case being about 20 litres/hr (measured at atmospheric pressure) and the gas pressure being 15.5 kg/cm² absolute (1518 kPa). After this pre-reduction stage the catalyst was at all times maintained in a hydrogen-containing atmosphere.

Example 9

The procedure of Example 8 was repeated using di-n-butyl oxalate at a feed rate of 30.6 mls/hr and a hydrogen flow rate of 284 litres/hr (measured at atmospheric pressure). The liquid condensate was shown to contain 0.25 wt% ethanol, 14.62 wt% n-butanol, 0.50 wt% n-butyl glycolate, 10.19 wt% ethylene glycol, and 75.73 wt% di-n-butyl oxalate. The observed conversion to ethylene glycol was 21.5% and the selectivity to ethylene glycol was 94.7%.

Example 10

The procedure of Example 8 was repeated using diethyl succinate at a feed rate of 15.4 ml/hr. The reactor pressure was 15.5 kg/cm² absolute (1518 kPa) and the inlet temperature was 242°C. The gas flow rate was 157.8 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.03 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

16.86 wt% ethanol
4.40 wt% tetrahydrofuran
0.8 wt% n-butanol
66.53 wt% diethyl succinate.



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This corresponds to a 32.2% conversion of diethyl succinate with a selectivity of 85.0% to tetrahydrofuran and 14.0% to n-butanol.

Example 11

The procedure of Example 8 was repeated using diethyl maleate at a feed rate of 16.9 ml/hr. The reactor pressure was 15.1 kg/cm² absolute (1484 kPa) and the inlet temperature was 222°C. The gas flow rate was 156.6 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.13 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

- 2.67 wt% tetrahydrofuran
- 8.49 wt% ethanol
- 0.4 wt% n-butanol
- 16.24 wt% diethyl succinate
- 64.08 wt% diethyl maleate.

This corresponds to a 22.2% conversion of diethyl maleate to tetrahydrofuran and n-butanol with a selectivity of 87.0% to tetrahydrofuran and 12.7% to n-butanol and a 15.6% conversion to diethyl succinate.

Example 12

The procedure of Example 8 was repeated using cyclohexyl acetate at a feed rate of 17.3 ml/hr. The reactor pressure was 15.5 kg/cm² absolute (1518 kPa) and the inlet temperature was 229°C. The gas flow rate was 157.2 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.15 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

- 1.14 wt% cyclohexane
- 1.36 wt% ethyl acetate
- 24.43 wt% ethanol
- 52.16 wt% cyclohexanol
- 7.86 wt% cyclohexyl acetate.

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This corresponds to a 92.8% conversion of cyclohexyl acetate.

Example 13

The procedure of Example 8 was repeated using benzyl acetate at a feed rate of 47.8 ml/hr. The reactor pressure was 16.9 kg/cm² absolute (1656 kPa) and the inlet temperature was 235°C. The gas flow rate was 466.2 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 3.19 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

0.42 wt% ethyl acetate
15.80 wt% ethanol
31.67 wt% toluene
1.90 wt% acetic acid
0.50 wt% benzyl alcohol,
41.33 wt% benzyl acetate

This corresponds to a 58.7% conversion of benzyl acetate with a selectivity of 98.5% to toluene.

Example 14

The procedure of Example 8 was repeated using methyl benzoate at a feed rate of 15.4 ml/hr. The reactor pressure was 15.5 kg/cm² absolute (1518 kPa) and the inlet temperature was 220°C. The gas flow rate was 156.6 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.03 hr⁻¹.

The condensate separated out into two layers and so no attempt at accurate analysis was made. However gas chromatography showed that the major products were toluene and methanol. It was estimated that approximately 40% conversion of methyl benzoate had been achieved, with only about 1% selectivity to benzyl alcohol.

Example 15

The procedure of Example 8 was repeated using ethyl



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phenylacetate at a feed rate of 16.7 ml/hr. The reactor pressure was 15.5 kg/cm² absolute (1518 kPa) and the inlet temperature was 215°C. The gas flow rate was 157.8 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.11 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

12.16 wt% ethanol
6.94 wt% ethyl benzene
21.50 wt% phenylethanol
53.04 wt% ethyl phenylacetate.

This corresponds to a 46.7% conversion of ethyl phenylacetate with a selectivity of approximately 100% to ethanol, 27.0% to ethylbenzene and 72.9% to phenylethanol.

Example 16

The procedure of Example 8 was repeated using ethylene glycol diacetate at a feed rate of 16.8 ml/hr. The reactor pressure was 28.0 kg/cm² absolute (2746 kPa) and the inlet temperature was 197°C. The gas flow rate was 240 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.12 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

0.63 wt% ethyl acetate
2.37 wt% ethanol
10.99 wt% ethylene glycol monoacetate
85.38 wt% ethylene glycol diacetate.

This corresponds to a 13.0% conversion of ethylene glycol diacetate, with a selectivity of 87.7% to ethanol, 12.2% to ethyl acetate, and 100% to ethylene glycol monoacetate.

Example 17

The procedure of Example 8 was repeated using ethyl lactate at a feed rate of 15.9 ml/hr. The reactor pressure was 16.4 kg/cm² absolute (1608 kPa) and the inlet

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temperature was 234°C. The gas flow rate was 156.6 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.06 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

12.62 wt% ethanol
0.25 wt% n-propanol
14.41 wt% 1,2-propanediol
64.49 wt% ethyl lactate.

This corresponds to a 34.7% conversion of ethyl lactate with a selectivity of 97.7% to 1,2-propanediol and 2.3% to n-propanol.

Example 18

The procedure of Example 8 was repeated using dimethyl adipate at a feed rate of 16.7 ml/hr. The reactor pressure was 29.5 kg/cm² absolute (2898 kPa) and the inlet temperature was 233°C. The gas flow rate was 240 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.11 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

4.92 wt% methanol
84.29 wt% dimethyl adipate
6.44 wt% 1,6-hexanediol

The condensate also contained some other unidentified compounds.

This corresponds to a 23.0% conversion of dimethyl adipate with a selectivity of approximately 100% to methanol and about 95% to 1,6-hexanediol.

Example 19

The procedure of Example 8 was repeated using t-butyl acetate at a feed rate of 18.3 ml/hr. The reactor pressure was 26.7 kg/cm² absolute (2622 kPa) and the inlet temperature was 200°C. The gas flow rate was 156.6 litres/hr (measured at atmospheric pressure). The liquid hourly space

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velocity was 1.22 hr^{-1} .

Gas chromatographic analysis showed the condensate to contain:-

19.87 wt% ethanol
3.18 wt% t-butanol
0.74 wt% ethyl acetate,
65.58 wt% t-butyl acetate
6.51 wt% water

This corresponds to a 56.5% conversion of t-butyl acetate. Although the selectivity to ethanol and t-butanol appears to be high, accurate assessment of selectivity was difficult because some of the t-butanol underwent dehydration to iso-butene which was detected as a product but not collected.

Example 20

The procedure of Example 8 was repeated using methyl methoxyacetate at a feed rate of 17.3 ml/hr. The reactor pressure was 29 kg/cm² absolute (2850 kPa) and the inlet temperature was 217°C. The gas flow rate was 157.2 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.15 hr^{-1} .

Gas chromatographic analysis showed the condensate to contain:-

22.23 wt% methanol
0.62 wt% ethanol
46.55 wt% 2-methoxyethanol
23.23 wt% methyl methoxyacetate
4.53 wt% methoxyethyl methoxyacetate.

This corresponds to a 77.6% conversion of methyl methoxyacetate with a selectivity of 2.0% to ethanol, 93.2% to methoxyethanol and 4.6% to methoxyethyl methoxyacetate.

Example 21

The procedure of Example 8 was repeated using methyl cyclohexanecarboxylate at a feed rate of 16.0 ml/hr. The reactor pressure was 14.8 kg/cm² absolute (1449 kPa)

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and the inlet temperature was 217°C. The gas flow rate was 156.0 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.07 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

11.80 wt% methanol
44.03 wt% cyclohexylmethanol
42.50 wt% methyl cyclohexanecarboxylate

This corresponds to a 57.8% conversion with a selectivity of approximately 100% to methanol and cyclohexanemethanol.

Example 22

The procedure of Example 8 was repeated using gamma-butyrolactone at a feed rate of 16.2 ml/hr. The reactor pressure was 28.8 kg/cm² absolute (2829 kPa) and the inlet temperature was 226°C. The gas flow rate was 156.0 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.08 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

12.40 wt% tetrahydrofuran
1.19 wt% n-butanol
12.19 wt% 1,4-butanediol
66.84 wt% gamma-butyrolactone.

This corresponds to a 47.6% conversion of gamma-butyrolactone with a selectivity of 53.2% to tetrahydrofuran, 41.8% to 1,4-butanediol and 5.0% to n-butanol.

Example 23

The procedure of Example 8 was repeated using gamma-butyrolactone at a feed rate of 16.0 ml/hr. The reactor pressure was 15.5 kg/cm² absolute (1518 kPa) and the inlet temperature was 215°C. The gas flow rate was 450 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.07 hr⁻¹.

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Gas chromatographic analysis showed the condensate to contain:-

0.02 wt% tetrahydrofuran
0.03 wt% n-butanol
9.17 wt% 1,4-butanediol
90.59 wt% gamma-butyrolactone.

This corresponds to a 9.4% conversion of gamma-butyrolactone with a selectivity of 97.4% to 1,4-butanediol.

Example 24

The procedure of Example 8 was repeated using gamma-butyrolactone at a feed rate of 15.4 ml/hr. The reactor pressure was 28.5 kg/cm² absolute (2794 kPa) and the inlet temperature was 217°C. The gas flow rate was 450 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.03 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

0.04 wt% tetrahydrofuran
0.04 wt% n-butanol
15.79 wt% 1,4-butanediol
83.96 wt% gamma-butyrolactone.

This corresponds to a 16.1% conversion of gamma-butyrolactone with a selectivity of 98.4% to 1,4-butanediol.

Example 25

The procedure of Example 8 was repeated using t-butyl formate at a feed rate of 64.1 ml/hr. The reactor pressure was 14.4 kg/cm² absolute (1414 kPa) and the inlet temperature was 170°C. The gas flow rate was 155.4 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 4.27 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

21.49 wt% methanol

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2.36 wt% methyl formate
64.50 wt% t-butanol
0.98 wt% t-butyl formate.

This corresponds to a 99% conversion of t-butyl formate. Accurate assessment of selectivity was not attempted. Iso-butene was also detected as a product, this being formed presumably by dehydration of t-butanol.

Example 26

The procedure of Example 8 was repeated using phenyl acetate at a feed rate of 17.1 ml/hr. The reactor pressure was 29.0 kg/cm² absolute (2850 kPa) and the inlet temperature was 222°C. The gas flow rate was 156.0 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 1.14 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

5.96 wt% ethanol
6.17 wt% ethyl acetate
24.69 wt% phenol
61.44 wt% phenyl acetate.

This corresponds to a 40.9% conversion of phenyl acetate with a selectivity of approximately 100% to phenol, 64.9% to ethanol and 35.1% to ethyl acetate.

Example 27

The procedure of Example 8 was repeated using methyl formate at a feed rate of 60.0 ml/hr. The reactor pressure was 8.6 kg/cm² absolute (842 kPa) and the inlet temperature was 194°C. The gas flow rate was 540 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 4.0 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

99.49 wt% methanol
0.22 wt% methyl formate.

This corresponds to a 99.7% conversion of methyl

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formate with a selectivity of 99.0% to methanol.

Example 28

The procedure of Example 8 was repeated using methyl formate at a feed rate of 180 ml/hr. The reactor pressure was 8.4 kg/cm² absolute (828 kPa) and the inlet temperature was 200°C. The gas flow rate was 540 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 12.0 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain:-

76.73 wt% methanol

23.10 wt% methyl formate.

This corresponds to a 76.9% conversion of methyl formate with a selectivity of 99.2% to methanol.

Example 29

The procedure of Example 8 was repeated using a mixture comprising 75 mol % methyl glycolate and 25 mol% methanol at a feed rate of 10.0 ml/hr. The reactor pressure was 28.1 kg/cm² absolute (2760 kPa) and the inlet temperature was 210°C. The gas flow rate was 155.4 litres/hr (measured at atmospheric pressure). The liquid hourly space velocity was 0.67 hr⁻¹.

Gas chromatographic analysis showed the condensate to contain a mixture of methanol, methyl glycolate, and ethylene glycol.

Calculations indicated a 13.7% conversion of methyl glycolate with a selectivity of approximately 98.0% to ethylene glycol.

Example 30

Using a procedure similar to that of Example 8 but with a catalyst volume of 50 ml. the hydrogenolysis of ethyl acetate was investigated using a crushed catalyst comprising a reduced mixture of 71.5% CuO and 18.5% ZnO. With a liquid feed rate of 21.7 ml/hr, corresponding to a space velocity of 0.43 hr⁻¹ and a 5 mol% ethyl acetate in hydrogen feed

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mixture. The conversion observed at 11.6 kg/cm² absolute (1138 kPa) and 150°C was 65.1% with essentially quantitative formation of ethanol. Under the same pressure and flow conditions at 200°C the observed conversion was 90.6%, also with essentially quantitative production of ethanol.

Example 31

When Example 30 was repeated using as catalyst a reduced mixture of 44.3% CuO, 46.3% ZnO and 9.4% AL₂O₃, the conversion at 150°C was 48.9% and at 200°C was 84.2%, in each case with essentially quantitative formation of ethanol.

CLAIMS

1. A process for effecting hydrogenolysis of a carboxylic acid ester which comprises contacting a mixture containing the ester and hydrogen with a hydrogenolysis catalyst at an elevated temperature characterised in that a vaporous mixture comprising the ester and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa).
2. A process according to claim 1, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).
3. A process according to claim 1 or claim 2, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 25 kg/cm² absolute (about 2453 kPa).
4. A process according to any one of claims 1 to 3, characterised in that the temperature is in the range of from about 180°C to about 240°C.
5. A process according to any one of claims 1 to 4, characterised in that the carboxylic acid ester is selected from esters of the general formula:

$$R(COOR')_n$$
 and $(R''''COO)_pR'''$
 wherein n and p each represent an integer of from 1 to about 5 and R, R', R'' and R''' each represent an optionally substituted saturated or unsaturated cyclic or acyclic hydrocarbon radical, one or more carbon atoms of which may be

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replaced by hetero atoms selected from nitrogen, oxygen and phosphorus.- -

6. A process according to claim 5, characterised in that each of R, R', R'', and R''' contains from 1 to about 12 carbon atoms.

7. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of formic acid and methanol is a product of hydrogenolysis.

8. A process according to claim 7, characterised in that the carboxylic acid ester is selected from methyl formate, iso-propyl formate, and t-butyl formate.

9. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of acetic acid and ethanol is a product of hydrogenolysis.

10. A process according to claim 9, characterised in that the carboxylic acid ester is selected from methyl acetate, ethyl acetate, sec-butyl acetate, t-butyl acetate, phenyl acetate, cyclohexyl acetate, and benzyl acetate.

11. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of butyric acid and n-butanol is a product of hydrogenolysis.

12. A process according to claim 11, characterised in that the carboxylic acid ester is n-butyl butyrate.

13. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of oxalic acid and ethylene glycol is a product of

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hydrogenolysis.

14. A process according to claim 13, characterised in that the carboxylic acid ester is di-n-butyl oxalate.

15. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of an acid selected from maleic acid, fumaric acid, acetylenedicarboxylic acid, and succinic acid and hydrogenolysis yields 1,4-butanediol and/or tetrahydrofuran.

16. A process according to claim 15, characterised in that the carboxylic acid ester is diethyl succinate or diethyl maleate.

17. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of phenylacetic acid and 2-phenylethanol is a product of hydrogenolysis.

18. A process according to claim 17, characterised in that the carboxylic acid ester is ethyl phenylacetate.

19. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of lactic acid and 1,2-propanediol is a product of hydrogenolysis.

20. A process according to claim 19, characterised in that the carboxylic acid ester is ethyl lactate.

21. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of adipic acid and 1,6-hexanediol is a product of hydrogenolysis.

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22. A process according to claim 21, characterised in that the carboxylic acid ester is dimethyl adipate.
23. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is a lactone and a diol is a hydrogenolysis product.
24. A process according to claim 23, characterised in that the carboxylic acid ester is gamma-butyrolactone and 1,4-butanediol is a hydrogenolysis product.
25. A process according to any one of claims 1 to 6, characterised in that the carboxylic acid ester is an ester of glycolic acid and ethylene glycol is a hydrogenolysis product.
26. A process according to claim 25, characterised in that the carboxylic acid ester is methyl glycolate.
27. A process according to any one of claims 1 to 26, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.
28. A process according to claim 27, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.
29. A process according to any one of claims 1 to 26, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by

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weight ZnO.

30. A process for the production of ethylene glycol which comprises effecting hydrogenolysis of an oxalic acid ester by contacting a mixture containing the ester and hydrogen with a hydrogenolysis catalyst at an elevated temperature characterised in that a vaporous mixture comprising the ester and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting ethylene glycol is recovered.

31. A process according to claim 30, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

32. A process according to claim 30 or claim 31, which characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

33. A process according to any one of claims 30 to 32, characterised in that the temperature is in the range of from about 180°C to about 240°C.

34. A process according to any one of claims 30 to 33, characterised in that the carboxylic acid ester is di-n-butyl oxalate.

35. A process according to any one of claims 30 to 34, characterised in that the catalyst comprises a reduced

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mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.

36. A process according to claim 35, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

37. A process according to any one of claims 30 to 34, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by weight ZnO.

38. A process for the production of methanol characterised in that a vaporous mixture containing a formic acid ester and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting methanol is recovered.

39. A process according to claim 38, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

40. A process according to claim 38 or claim 39, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

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41. A process according to any one of claims 38 to 40, characterised in that the temperature is in the range of from about 130°C to about 220°C.

42. A process according to any one of claims 38 to 41, characterised in that the formic acid ester is selected from methyl formate, iso-propyl formate, and t-butyl formate.

43. A process according to any one of claims 38 to 42, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.

44. A process according to claim 43, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

45. A process according to any one of claims 38 to 42, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by weight ZnO.

46. A process for the production of ethanol characterised in that a vaporous mixture containing an acetic acid ester and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting ethanol is recovered.

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47. A process according to claim 46, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

48. A process according to claim 46 or claim 47, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

49. A process according to any one of claims 46 to 48, characterised in that the temperature is in the range of from about 180°C to about 240°C.

50. A process according to any one of claims 46 to 49, characterised in that the acetic acid ester is selected from methyl acetate, ethyl acetate, sec-butyl acetate, and t-butyl acetate.

51. A process according to any one of claims 46 to 50, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.

52. A process according to claim 51, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

53. A process according to any one of claims 46 to 50, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by

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weight ZnO.

54. A process for the production of 1,4-butanediol and/or tetrahydrofuran characterised in that a vaporous mixture containing an ester of an acid selected from maleic acid, fumaric acid, acetylene-dicarboxylic acid, and succinic acid and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting 1,4-butanediol and/or tetrahydrofuran is recovered.

55. A process according to claim 54, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

56. A process according to claim 54 or claim 55, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

57. A process according to any one of claims 54 to 56, characterised in that the temperature is in the range of from about 180°C to about 240°C.

58. A process according to any one of claims 54 to 57, characterised in that the ester is diethyl maleate.

59. A process according to any one of claims 54 to 58, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by



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weight ZnO.

60. A process according to claim 59, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

61. A process according to any one of claims 54 to 58, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by weight ZnO.

62. A process for the production of ethylene glycol characterised in that a vaporous mixture containing a glycolic acid ester and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting ethylene glycol is recovered.

63. A process according to claim 62, characterised in that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

64. A process according to claim 62 or claim 63, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 35 kg/cm² absolute (about 3435 kPa).

65. A process according to any one of claims 62 to 64, characterised in that the temperature is in the range of from

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about 180°C to about 240°C.

66. A process according to any one of claims 62 to 65, characterised in that the glycolic acid ester is methyl glycolate.

67. A process according to any one of claims 62 to 66, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.

68. A process according to claim 67, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

69. A process according to any one of claims 62 to 66, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by weight ZnO.

70. A process for the production of 1,4-butanediol characterised in that a vaporous mixture containing butyrolactone and hydrogen is contacted with a catalyst comprising a reduced mixture of copper oxide and zinc oxide at a temperature in the range of from about 75°C up to about 300°C and at a pressure in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) up to about 100 kg/cm² absolute (about 9813 kPa), and resulting 1,4-butanediol is recovered.

71. A process according to claim 70, characterised in

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that the pressure is in the range of from about 0.1 kg/cm² absolute (about 9.8 kPa) to about 50 kg/cm² absolute (about 4906 kPa).

72. A process according to claim 70 or claim 71, characterised in that the pressure is in the range of from about 5 kg/cm² absolute (about 491 kPa) to about 45 kg/cm² absolute (about 4416 kPa).

73. A process according to any one of claims 70 to 72, characterised in that the temperature is in the range of from about 180°C to about 240°C.

74. A process according to any one of claims 70 to 73, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 10 to about 70 percent by weight CuO and about 90 to about 30 percent by weight ZnO.

75. A process according to claim 74, characterised in that the mixture comprises from about 20 to about 40 percent by weight CuO and from about 60 to 80 percent by weight ZnO.

76. A process according to any one of claims 70 to 73, characterised in that the catalyst comprises a reduced mixture of copper oxide and zinc oxide derived from a mixture comprising, before reduction, from about 65 to about 85 percent by weight CuO and about 15 to about 35 percent by weight ZnO.

77. The product of a process according to any one of claims 1 to 76.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 82/00118

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ³ : C 07 B 1/00; C 07 C 29/136; C 07 C 29/17; C 07 C 31/00; C 07 C 31/20; C 07 C 33/22; C 07 D 307/08 //B 01 J 23/80																										
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Classification System IPC³ </div> </td> <td style="border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Classification Symbols C 07 B 1/00; C 07 C 29/00; B 01 J 23/00 </div> </td> </tr> </table> <div style="border: 1px solid black; padding: 5px; margin-top: 5px; text-align: center; font-size: small;"> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵ </div>			<div style="border: 1px solid black; padding: 5px;"> Classification System IPC³ </div>	<div style="border: 1px solid black; padding: 5px;"> Classification Symbols C 07 B 1/00; C 07 C 29/00; B 01 J 23/00 </div>																						
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; font-size: small;">Category ⁶</th> <th style="width: 70%; font-size: small;">Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 20%; font-size: small;">Relevant to Claim No. ¹⁸</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">X</td> <td>DE, B, 1203254 (DEHYDAG) 21 October 1965 see example 1; claim 1 --</td> <td style="text-align: center;">1,4,5,6</td> </tr> <tr> <td style="text-align: center;">X</td> <td>FR, A, 16000072 (HENKEL) 28 August 1970 see page 5, "Catalyst preparation B", example 3; abstract --</td> <td style="text-align: center;">1,4,5,6</td> </tr> <tr> <td style="text-align: center;">X</td> <td>DE, A, 2455617 (BASP) 26 May 1976 see page 10, "Catalyst preparation 2" example 2; claims 1c and 3 --</td> <td style="text-align: center;">1,4,23,24, 70-76</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>DE, B, 1005497 (DEHYDAG) 4 April 1957 see example 3, claim --</td> <td style="text-align: center;">1,4,5</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>FR, A, 1303231 (VEB) 30 July 1962 see example 3, abstract 1-3 --</td> <td style="text-align: center;">1-22</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>BE, A, 622053 (HOECHST) 4 March 1963 see claims --</td> <td style="text-align: center;">1-6</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 2285448 (D.J. LODER) 9 June 1942 see page 1, right-hand column, lines 32-52; claims; examples 1,2</td> <td style="text-align: center;">1,4-6,25,26 62-69</td> </tr> </tbody> </table> <div style="font-size: x-small; margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>• Special categories of cited documents: ¹³</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div> </div>			Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸	X	DE, B, 1203254 (DEHYDAG) 21 October 1965 see example 1; claim 1 --	1,4,5,6	X	FR, A, 16000072 (HENKEL) 28 August 1970 see page 5, "Catalyst preparation B", example 3; abstract --	1,4,5,6	X	DE, A, 2455617 (BASP) 26 May 1976 see page 10, "Catalyst preparation 2" example 2; claims 1c and 3 --	1,4,23,24, 70-76	Y	DE, B, 1005497 (DEHYDAG) 4 April 1957 see example 3, claim --	1,4,5	Y	FR, A, 1303231 (VEB) 30 July 1962 see example 3, abstract 1-3 --	1-22	Y	BE, A, 622053 (HOECHST) 4 March 1963 see claims --	1-6	Y	US, A, 2285448 (D.J. LODER) 9 June 1942 see page 1, right-hand column, lines 32-52; claims; examples 1,2	1,4-6,25,26 62-69
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US, A, 2248465 (W. RITTMEISTER) 8 July 1941 --	1-77
A	DE, A, 2613226 (HENKEL) 29 September 1977 --	1-77
A	LU, A, 44814 (C.H. HOOD et al.) 14 January 1964 --	1-77
A	CH, A, 348957 (VEREINIGTE GLANZSTOFF-FABRIKEN) 15 November 1960 --	1-77
A	FR, A, 2418025 (CHEVRON) 21 September 1979 --	1-77
A	FR, A, 2388780 (CHEVRON) 24 November 1978 (cited in the application) & US, A, 4113662 (CHEVRON) 12 September 1978 --	1-77
A	US, A, 3197418 (K. MAEBASHI et al.) 27 July 1965 (cited in the application) --	1-77
L	US, A, 4112245 (L. CISTERNI) 5 September 1978 (cited in the application) -----	1

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